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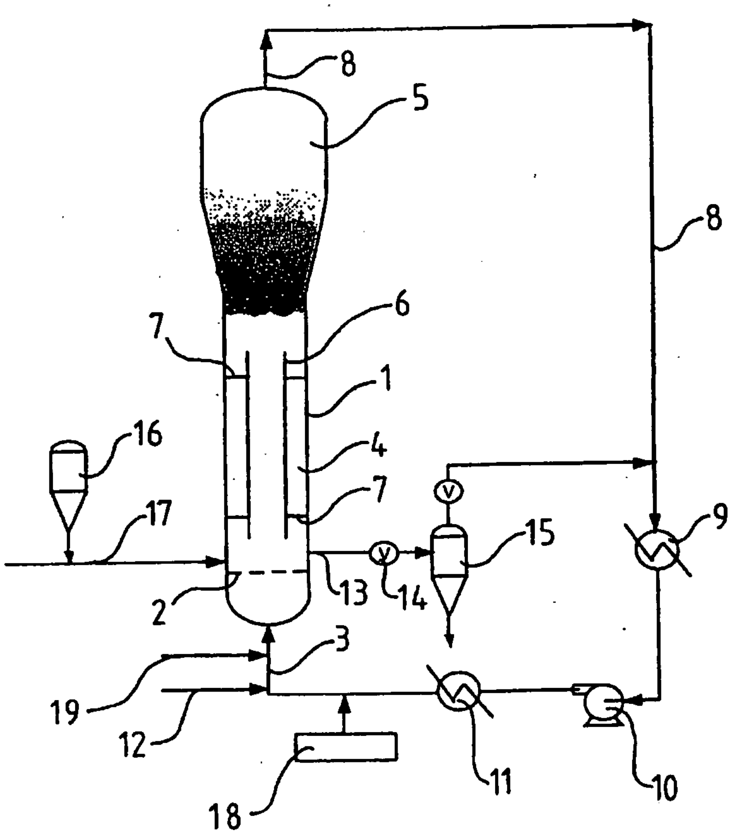
(54) **Title:** FLUIDISED BED REACTOR



(57) Abstract: Fluidised bed reactor process for the polymerisation of one or more monomers, wherein the reactor comprises a reaction zone which is confined at the underside by a gas distribution plate and at the top side by a virtual end surface, in which, under operating conditions, a fluidised bed is maintained between the underside and the top side, said reactor zone being divided into two or more compartments by one or more substantially vertical partition walls extending from a point located above the gas distribution plate to a point located below the end surface.

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FLUIDISED BED REACTOR

The invention relates to a process for the polymerisation of one or more monomers in a fluidised bed reactor, which reactor comprises a reaction zone which is confined at the underside by a gas distribution plate and at the top side by a virtual end surface, in which a fluidised bed is maintained between the underside and the top side and in which at least part of the gaseous stream withdrawn from the top of the reactor is cooled to a temperature above the condensation temperature of said stream, and in which at least part of the resulting gas stream is recycled to a reactor via a gas inlet below the gas distribution plate.

Gas-phase fluidised bed polymerisation of one or more monomers, like an olefin or olefins, is effected in a usually vertical elongated reactor in which a bed of polymer particles is maintained in fluidised condition with the aid of an ascending gas stream which contains at least the gaseous monomer(s) to be polymerised. The gas stream is passed through a gas distribution plate which separates the lower part of the reactor from the reaction zone proper. In this plate there are provided perforations that suitably distribute the gas stream supplied over the reaction zone. A peripheral section of the gas distribution plate may be sealed so as to obtain a particular pressure drop at a lower flow rate of the gas. In order to prevent polymer particles from building up on such peripheral section, the seal is preferably designed as an inclined wall which extends from the gas distribution plate to the wall of the reactor. The angle of the inclined wall to the gas distribution plate must be greater than the angle of natural repose of the polymer particles in the reactor and, furthermore, is generally at least 30°, preferably at least 40° and more preferably is between 45° and 85°.

The ascending gas stream may optionally contain one or more inert gases and for example hydrogen as a chain length regulator. An important objective of the addition of inert gases is to control the dew point of the gas mixture. Suitable inert gases are for example inert hydrocarbons such as ethane, propane, but also nitrogen. Such an inert gas may be added to the gas stream as a gas or, in condensed form, as a liquid.

The gas stream is discharged through the top of the reactor and,

after certain processing operations, fresh monomer is added to it to make up for the monomer(s) consumed in the polymerisation, and then the gasstream is again supplied to the reactor as (a portion of) the ascending gas stream in order to maintain the bed.

A catalyst is also added to the bed. During the process, under the influence of the catalyst present, fresh polymer is continuously formed and at the same time polymer that has formed is withdrawn from the bed, with the bed volume and mass being kept substantially constant.

The polymerisation is an exothermic reaction. Heat needs to be removed continuously so as to keep the temperature in the reactor at the desired level. Such removal is effected via the gas stream which leaves the reactor at a higher temperature than that at which it is supplied to the reactor. The superficial gas velocity in the reactor cannot be chosen to be arbitrarily large and so no arbitrarily large amount of heat can be removed. The minimum velocity is dictated by the requirement for the bed to remain fluidised. On the other hand, the velocity must not be so large that a significant amount of polymer particles are blown out through the top of the reactor. The aforementioned limits are heavily dependent on the density and viscosity of the gas as well as on the dimensions and the density of the polymer particles present in the bed, and can be determined by experiment. Practical values for the superficial gas velocity are between 0.05 and 1.0 m/sec. These requirements limit the maximum flow rate of the gas stream at the given reactor dimensions and, thus, the maximum attainable heat removal. The maximum allowable amount of heat of reaction produced, and hence the maximum amount of polymer to be produced, are limited likewise.

The detailed design and operation of fluidised bed reactors for the polymerisation of one or more olefin monomers and suitable process conditions are known per se and are described in detail in for example EP-A-21,605. From this EP-A-21,605 it is known to replenish the gas stream discharged from the reactor with fresh monomer(s) and to cool it to a temperature above the condensation temperature of said stream (the so-called "non-condensed mode"). The cooled gas stream so obtained is recycled to the bottom of the reactor. The dew point of the cooled recycle stream must be lower than the temperature in the reaction zone so that essentially no liquid will condensate in it.

The present invention relates to a process for the polymerisation

of one or more monomers in a specific fluidised bed reactor, which reactor, at given dimensions, allows a more even reactor temperature and an improved stability of the reactor than of a reactor according to the prior art, both in cases where the reactors are operated under "non-condensed mode conditions".

This object is achieved by a process in which the reaction zone of the reactor is divided into two or more compartments by one or more substantially vertical partition walls extending from a point located above the gas distribution plate to a point located below the end surface.

It has been found that when in such a reactor a fluidised bed is maintained that extends, both at the top and bottom, beyond the partition walls, so that the partition walls are submerged in the fluidised bed, a more even reactor temperature over the bed is achieved, which permits a higher reactor temperature so allowing higher polymer production rates at equal reactor dimensions. It is now possible to allow for larger polymer particles in the fluidized bed. Next to that, less fouling of the reactor has been observed.

In a reactor according to the prior art the ratio of the height of the fluidised bed to the diameter of the radial cross section (H/D-ratio) usually is 3 to 5 at the most. At higher ratios it has proved impossible to maintain a stable fluidised bed.

An additional advantage of a reactor having at least one partition wall is that it is now possible to choose a higher H/D-ratio for the reactor, for instance, an H/D-ratio of greater than 5, and even up to 20, which is much higher than in the case of the known reactors, while yet maintaining a stable fluidised bed, resulting in a more controlled polymerisation process. This advantage presents major engineering advantages for polymerisation reactors because they are pressure vessels.

A particularly suitable partition wall in the reactor of the invention is a pipe or hollow section placed in vertical position, preferably concentric with the reactor. Since the pipe or hollow section is completely submerged in the fluidised bed, no appreciable pressure differences occur across the wall of the pipe so that the pipe may be of light-duty construction. This applies also to walls of different shapes.

The walls can simply be suspended from a higher section of the reactor, supported by a bottom section or secured to the wall of the reactor. In the present context a hollow section differs from a pipe in terms of the shape of its

cross section. The cross section of a pipe is curved, for example circular or elliptical, whilst that of a hollow section is angular, for example triangular, rectangular, octagonal or with more angles, with or without the angles being uniform. The hollow section or the pipe may have a uniform and/or tapered cross-section, for instance a conical shape, including tapering inwardly and outwardly, for instance, in a hyperbolic shape. For conical shapes, it is preferred that the apex angle formed by the walls of pipe or hollow section is generally not more than 5°, preferably not more than 2.5°. Particularly suitable are angles between 0° and 2°. The ratio of the area of the radial cross section of the pipe or hollow section to that of the reactor is between 1:9 and 9:10 and, in order to achieve as high a stability as possible, preferably between 1:5 and 3:4. In the case of a conical pipe or hollow section, the same applies to the average cross-sectional area thereof. The lower end of the pipe or hollow section is located at least 0.1 x the diameter of the reaction zone above the gas distribution plate and preferably 3 x that diameter at the most. If the dimensions given here are departed from, the favourable effect of the presence of a vertical partition wall is diminished. The upper end is located at least 0.1 x the diameter of the reaction zone below the end of that reaction zone and preferably not more than 3 x that diameter. It has been found that it is far less critical for the bed to extend further beyond the partition wall at the upper end than at the lower end. The upper end of the partition wall may be lower accordingly as the H/D-ratio of the fluid bed increases. What is stated here on the positioning of the wall in the reaction zone applies also to the vertical partition walls to be explained below.

Another embodiment of a suitable partition wall is a substantially axially oriented flat, curved or folded plate present in the reaction zone. It is preferred for such a partition wall to connect to the inner wall of the reactor although a clearance of up to 10 cm in-between is permissible. In this way, the reaction zone is divided into two or more compartments, which may be differently sized. The area ratio of the radial cross section of a compartment to the radial cross section of the reactor preferably is between 0.1 and 0.9 and more preferably between 0.20 and 0.75. The substantially axially oriented wall should be virtually vertical. This should be understood to mean parallel with the axis of the reactor in its vertical position but also out of parallel by not more than 5°, preferably not more than 2.5°.

Introducing fresh monomer(s) via several inlets at different heights of the reactor gives the possibility to vary the reaction conditions, as a result of which the operating window of the polymerisation reaction is improved and therefore broadening the product capabilities of the fluidised bed reactor.

The supplied amount of gas includes, besides the gas supplied via the recycle stream, all other gases supplied to the reactor, including at least the propellant and carrier gases that are employed in introducing the catalyst, a catalyst activator and/or other substances desired or needed for the polymerisation.

The process according to the present invention is suitable for any kind of exothermic polymerization reaction in the gas phase. Suitable monomer include olefin monomers, polar vinyl monomers, diene monomers and acetylene monomers. The process of the present invention is especially suitable for the manufacture of polyolefins by the polymerisation of one or more olefin monomers, at least one of which is preferably ethylene or propylene. Preferred olefin monomers for use in the process of the present invention are those having from 2 to 8 carbon atoms. However, small quantities of olefin monomers having more than 8 carbon atoms, for example 9 to 18 carbon atoms, can be employed if desired. Thus, in a preferred mode, it is possible to produce homopolymers of ethylene and/or propylene or copolymers of ethylene or propylene with one or more C_2-C_8 alpha-olefin monomers. The preferred alpha-olefin monomers are ethylene, propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, and octene-1. An example of a higher olefin monomer that can be copolymerised with the primary ethylene and/or propylene monomer, or as partial replacement for the C_2-C_8 monomer is decene-1. Also dienes are suitable, like 1,4-butadiene, 1,6-hexadiene, dicyclopentadiene, ethylidene norbornene and vinyl norbornene.

When the process is used for the copolymerisation of ethylene and/or propylene with other alpha-olefin monomers the ethylene and/or propylene are present as the major component of the copolymer, and preferably are present in an amount at least 70 wt %, more preferably 80 wt % of the total monomers.

The process is particularly suitable for polymerising olefin monomers at a pressure of between 0.5 and 10 Mpa, preferably between 1 and 5 Mpa, and and at a temperature of between 30°C and 130°C, and particularly between 45°C and 110°C.

The polymerisation reaction may be carried out in the presence of any catalyst system known in the art (for instance, anionic catalyst, cationic catalyst or free-radical catalyst) suited for the gas phase polymerisation of one or more (olefin) monomers, like a catalyst system of the Ziegler-Natta type, consisting of a solid catalyst essentially comprising a compound of a transition metal and of a cocatalyst comprising an organic compound of a metal (i.e. an organometallic compound, for example an alkylaluminium compound); also so-called single site catalyst systems, like metallocene based catalyst systems, are suitable.

The catalyst may also be in the form of a prepolymer powder prepared in a prepolymerisation stage with the aid of a catalyst system described above. The prepolymerisation may be carried out by any known process, for example, polymerisation in a liquid hydrocarbon diluent or in the gas phase using a batch process, a semi-continous process or a continous process.

The invention also relates to a reactor system, suitable for carrying out the process of the present invention. Such a reaction system comprises a fluidised bed reactor, having at the underside a gas distribution plate, having means for the supply of reaction ingredients, having means for withdrawal of a gaseous stream from the top of the reactor, having a cooler for cooling said gaseous stream to a temperature above the condensation temperature of said stream, and having means for recirculating the stream out of the cooler to the reactor.

Such a reactor system is known from the art cited above.

The aim of the invention is to provide a reactor system, in which a process for the polymerisation of one or more (olefin) monomers is possible, in which system a more even reaction temperature can be achieved, as well as an improved reactor stability.

This is achieved in a reactor system, wherein in the reactor the reaction zone is divided into two or more compartiments by one or more substantially vertical partition walls, extending from a point located above the gas distribution plate to a point located below the virtual end surface of the fluidised bed under polymerisation conditions.

In particular, said partition wall is a pipe or hollow section, preferably concentric with the reactor. The preferred configurations of the reactor system of the invention are described in greater detail earlier in this specification.

In particular, the reactor system of the present invention comprises means for recirculating the stream out of the cooler to the reactor.

It should also be appreciated that the present invention is suitable for retrofitting existing reactors by installing one or more partition walls, pipes or hollow sections into the reactor. In particular, a reactor could be retrofitted by installing a pipe, as discussed above, by fixing the pipe to an internal section of the reactor.

The invention is applicable both for so-called "grass-root" installations as well as for debottlenecking existing fluidised bed polymerisation installations. In the last case the full benefit of the invention might not be obtainable, as the capabilities of other units in the total polymerisation system may form a constraint on the maximum productivity of the system. (In other words: the throughput of the polymerisation system as a whole might be hindered by constraints in the system other than in the reactor section.) In situations where a new, integrated, polymerisation process is designed and built ("grass root"), the benefits of the present invention can be fully used and exploited.

The invention is elucidated by means of the following drawings, which are not intended to limit the boundaries of the invention.

Fig. 1 is an arrangement for polymerising one or more monomers, which includes a first embodiment of the process of the present invention with a reactor having a tubular partition wall and with a common inlet for gas below a gas distribution plate;

Fig. 2 is an arrangement as in Fig. 1, in which the tubular partition wall has a conical shape;

Fig. 3 is an arrangement as in Fig. 1 with a vertical plate serving as partition wall;

Fig. 4 is a radial cross section of the reactor in Fig. 1 along line A-A; and

Fig. 5 is a similar cross section of a reactor in which a folded vertical plate serves as partition wall.

Fig. 1 shows a reactor body in the form of a vertical cylinder in which 2 is a gas distribution plate which brings about the desired distribution of the fluidising gas introduced into the reactor below the gas distribution plate 2 through feed line 3. In the reaction zone proper 4 the gas stream introduced maintains above the gas distribution plate 2 a fluidised bed of growing polymer particles which extends to below or even to the bottommost part of velocity-reducing zone 5. A cylindrical pipe 6 is concentrically suspended in reaction zone 4 from the wall

of reactor 1 with supports 7. Pipe 6 is submerged in the fluidised bed. Zone 5 widens relative to reaction zone 4. In this zone 5 the gas velocity decreases to the point where the gas is unable to substantially entrain any further the polymer particles that have formed in the reaction zone. As a consequence, the recycle stream discharged through discharge line 8 is virtually free from entrained polymer particles. The recycle stream is cooled in heat exchanger 9, compressed in compressor 10 and cooled in heat exchanger 11 to a temperature above the condensation temperature of said stream. Make-up monomer(s) is (are) added to this cooled recycle stream through line 12, whereupon the mixture is reintroduced at the bottom of the reactor through line 3. A polymer-gas stream is discharged from the reactor through drain line 13, which can be closed by valve 14. This stream is separated into polymer and gaseous components in separator 15. The polymer is discharged from separator 15 through the bottom and is processed further. Such further processing may involve processes that are known per se and are not shown in the figure, like removal of absorbed or dissolved liquid.

The gaseous components, on being pressurised to the required pressure, are added to the recycle stream in line 8 (not shown in the figure). Besides the monomer, the required catalyst system and, optionally, a catalyst activator are supplied to the reactor. Here, too, the catalyst system is preferably supplied directly to the fluidised bed above the gas distribution plate from storage vessel 16 and propelled by an (inert) gas through line 17, which also terminates below the lower end of pipe 6. The activator can be added to the feed stream in line 3 via metering device 18. If necessary, a propellant is also added to this stream via feed line 19.

In Fig. 2, contrary to Fig. 1, pipe 206 has a conical shape with an apex angle of 1.5°. The conical shape is shown exaggerated in the purpose of clarity.

In Fig. 3, 340 is a vertical plate which serves as a partition wall to divide the reactor 301 into two unequal compartments 341 and 342. A bird's eye view of this is shown in Fig. 4. Catalyst feed line 317 terminates in compartment 341. A gas-impervious screen 343 extends from gas distribution plate 302 along the inner circumference of the reactor to the reactor wall at an angle to the plate of 50°.

CLAIMS

1. Process for the polymerisation of one or more monomers in a fluidised bed reactor, which reactor comprises a reaction zone which is confined at the underside by a gas distribution plate and at the top side by a virtual end surface, in which a fluidised bed is maintained between the underside and the top side, and in which at least part of the gaseous stream withdrawn from the top of the reactor is cooled to a temperature above the condensation temperature of said stream and in which at least part of the resulting gas stream is recycled to the reactor via a gas inlet below the gas distribution plate, characterised in that the reaction zone of the reactor is divided into two or more compartments by one or more substantially vertical partition walls extending from a point located above the gas inlet to a point located below the end surface.
2. Process according to Claim 1, characterised in that the partition wall has the shape of a pipe or hollow section.
3. Process according to Claim 2, characterised in that the pipe or hollow section is concentric with the reaction zone.
4. Process according to Claim 1, characterised in that the partition wall is a substantially axially oriented flat, curved or folded plate.
5. Process according to any one of Claims 1-4, characterised in that the H/D-ratio of the fluid bed is greater than 5.0.
6. Process according to anyone of Claims 1-5, characterised in that at least one of the monomers is ethylene or propylene.
7. Process according to anyone of Claims 1-6, characterised in that the polymerisation is performed at a pressure of between 0.5 and 10 MPa.
8. Process according to anyone of Claims 1-7, characterised in that the polymerisation is performed at a temperature of between 30 and 130°C.
9. Reactor system, suitable for polymerising one or more monomers, comprising a fluid bed reactor, having at the underside a distribution plate inlet, having means for the supply of reaction ingredients, having means for the withdrawal of a gaseous stream from the top of the reactor, having a cooler for cooling said gaseous stream to a temperature above the

condendation temperature of said stream, and having means for recirculating the stream out of the cooler to the reactor, characterised in that in the reactor the reaction zone is divided into two or more compartiments by one or more substantially vertical partition walls, extending from a point above the gas distribution plate.

10. Reactor system according to Claim 9, characterised in that the partition wall is a pipe or hollow section.

11. Reactor system according to Claim 10, characterised in that the pipe or hollow section is concentric with the reactor.

12. Reactor system according to anyone of Claims 9-11, characterised in that the H/D-ratio of the reactor is greater than 5.

13. Reactor system according to anyone of Claims 9-12, characterised in that the ratio of the area of the radial cross section of the pipe or hollow section to that of the reactor is between 1:5 and 3:4.

14. Reactor system according to Claim 9, characterised in that the partition wall is a substantially axially oriented flat, curved or folded plate.

15. Reactor system according to anyone of Claims 9-14, characterised in that the reactor system comprises means for recirculating the stream out of the cooler to the reactor as a gas mixture.

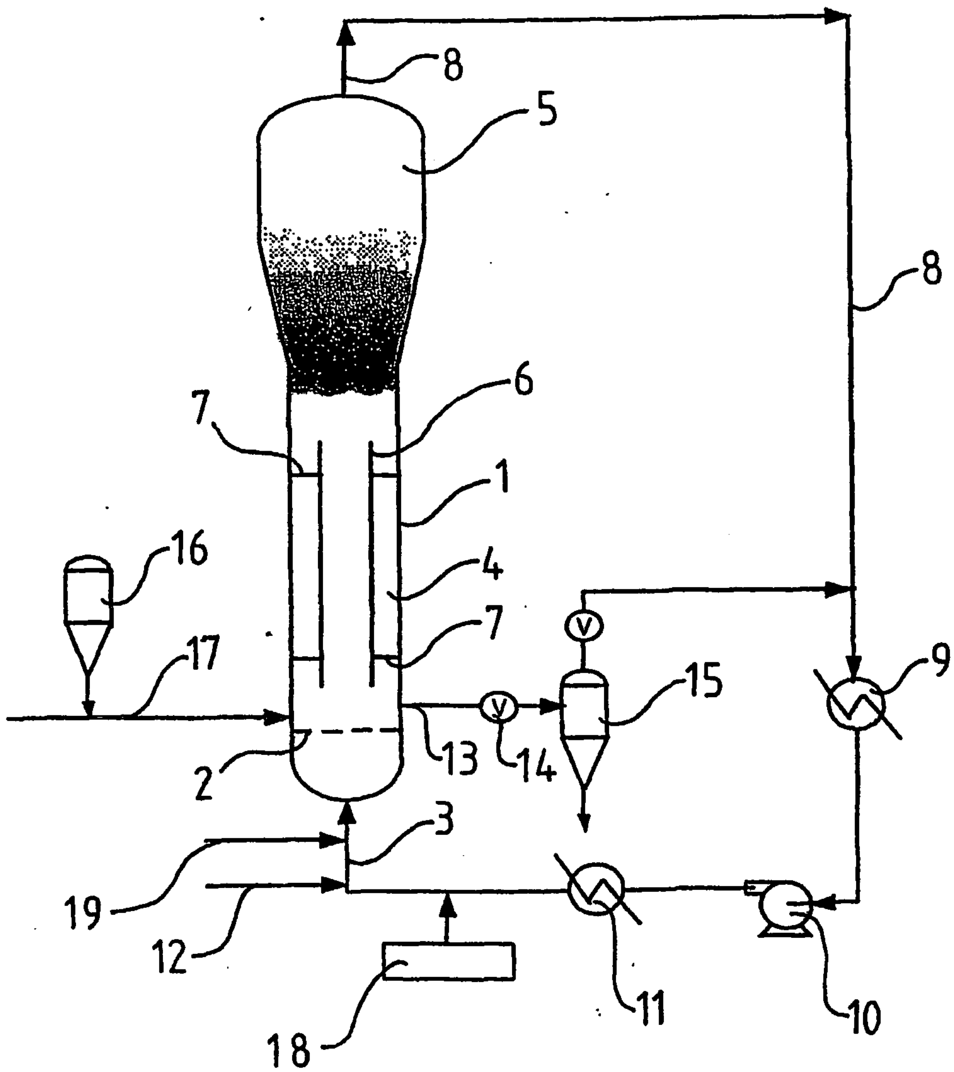

Fig. 1

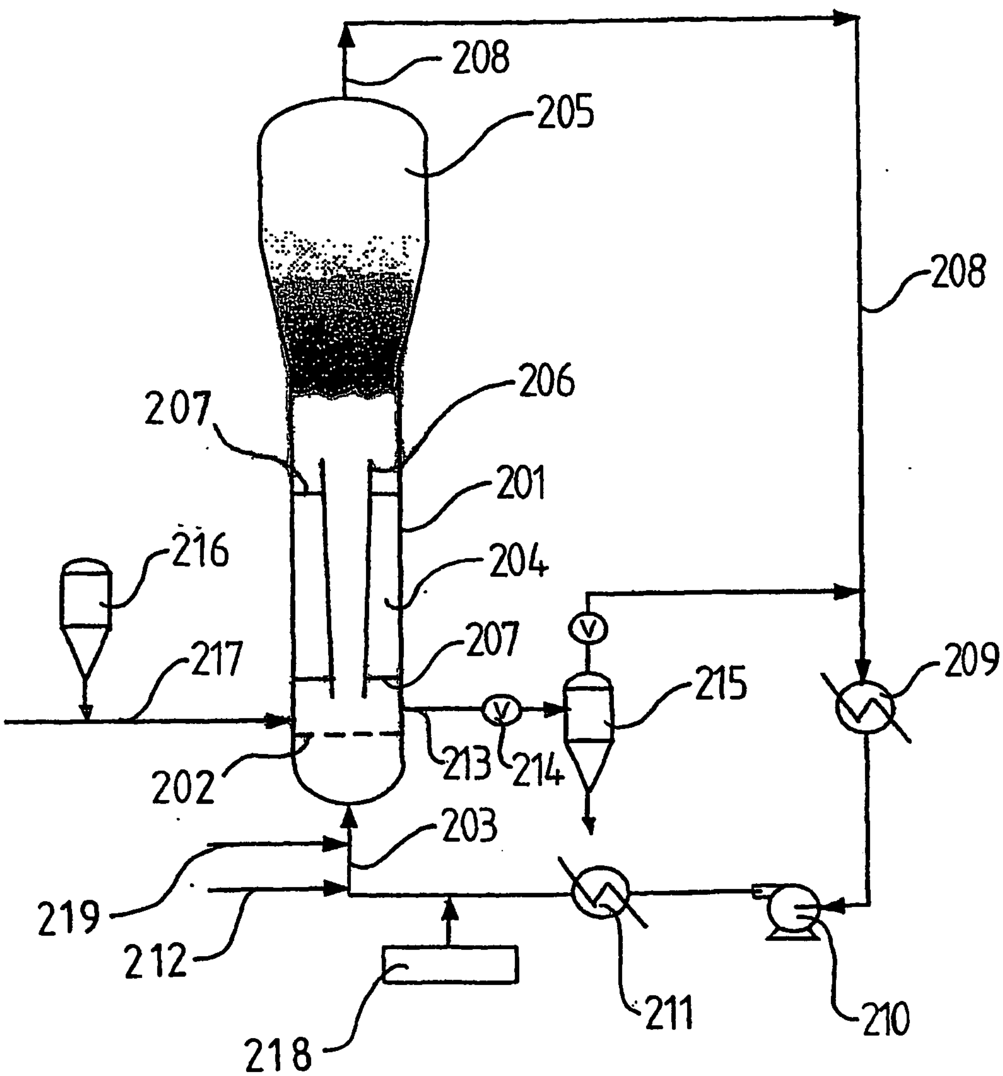
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Fig. 2

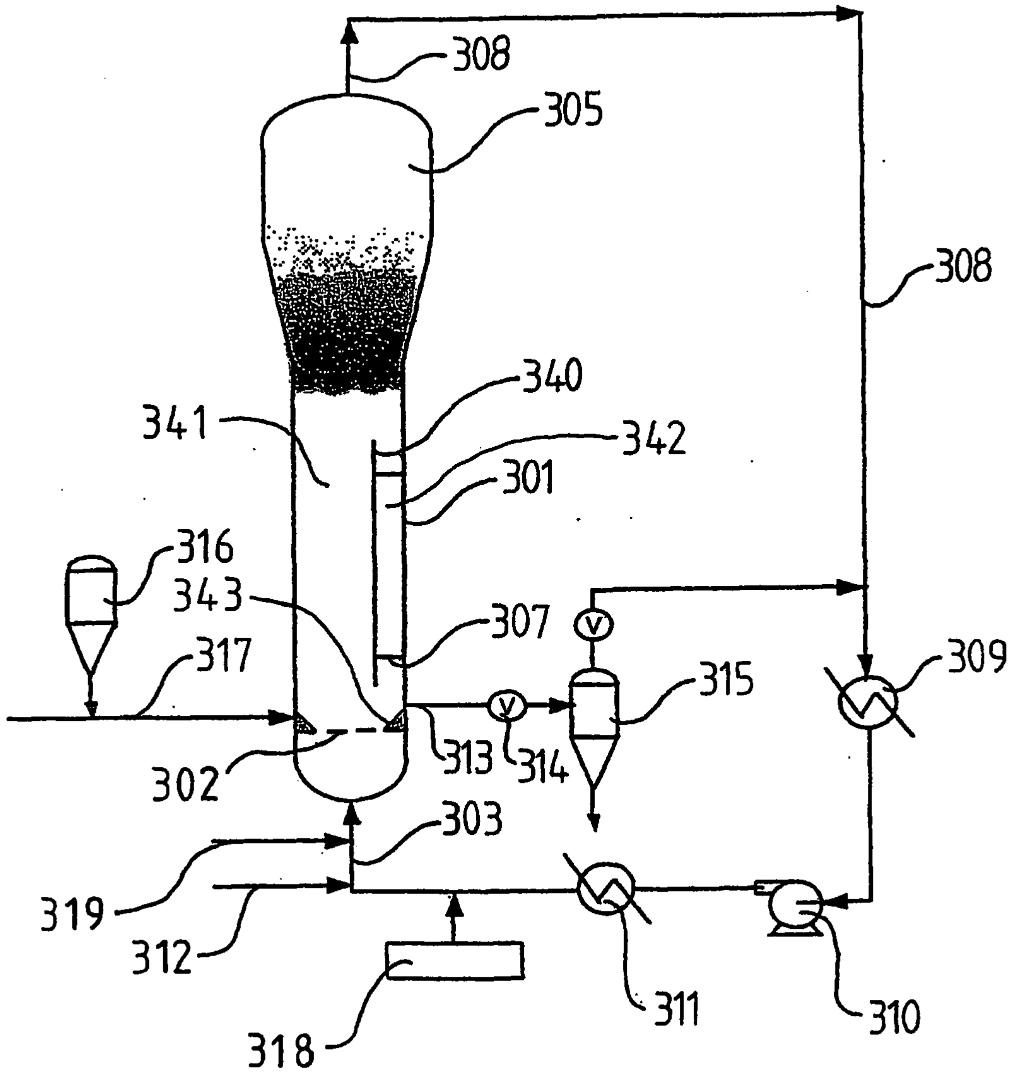
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Fig. 3

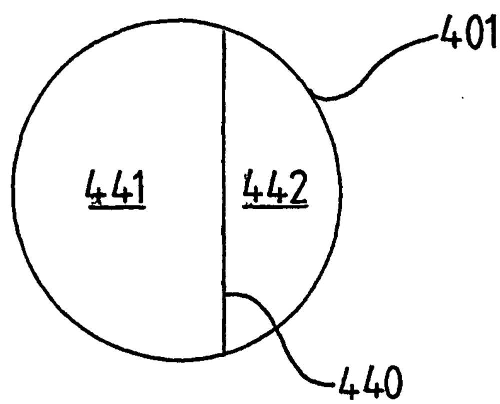

Fig. 4

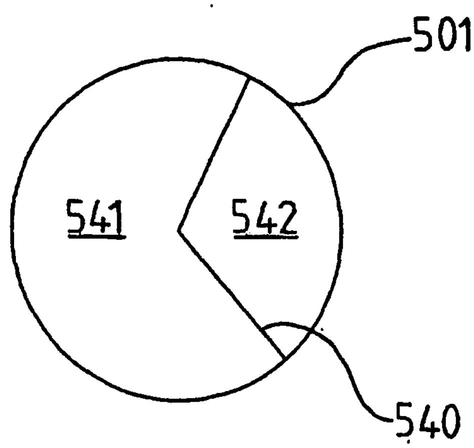

Fig. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 00/00833

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F2/34 C08F2/01 C08F10/00 B01J8/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 69552 A (DSM NV ;MUSTERS STANISLAUS MARTINUS PE (NL)) 23 November 2000 (2000-11-23) claims 12-19; figures	9-15
A	EP 0 301 872 A (BP CHEM INT LTD) 1 February 1989 (1989-02-01) claims; figures	1-15
X	US 5 114 700 A (MEIHACK WOLFGANG F A T ET AL) 19 May 1992 (1992-05-19)	9-15
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X	US 5 169 913 A (STAFFIN H KENNETH ET AL) 8 December 1992 (1992-12-08) claims; figures	1-15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 July 2001	19/07/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kaumann, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 00/00833

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 446 059 A (BP CHEMICALS SNC ;BP CHEM INT LTD (GB)) 11 September 1991 (1991-09-11) column 6, line 4 - line 19 column 14, line 6 - line 31; claims; figures	1-15
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A	GB 2 254 574 A (TAMPELLA POWER OY) 14 October 1992 (1992-10-14) figure 1	9

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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